Growth and Nano-structural Studies of Metallic Multilayers for X-ray Mirrors

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All praises for Allah who is the entire source of knowledge and wisdom endowed to mankind and all respect for The Holy Prophet (PBUH) who is forever a torch of guidance.
Abstract

A part of the Ph.D. project focused on growth and characterization of metal multilayers is presented in this licentiate thesis. The main interest in carrying out this research is to develop highly reflective normal-incidence condenser mirrors for soft X-ray microscopy studies in the water window ($\lambda = 2.4 - 4.2$ nm) wavelength regime.

Transition metals like Sc, Ti, V, etc. have been considered because of the presence of their $2p$-absorption edges within the water window. An anomalous dispersion at absorption edges has been utilized to get enhanced reflectance of soft X-rays. Since a single surface exhibits a very poor X-ray reflectivity, Cr/Sc, Cr/Ti, and Ni/V multilayers were grown in order to coherently add many reflections from several interfaces. The selection of Cr and Ni, as spacer layer, was made on the basis of their X-ray optical contrasts with the above-mentioned transition metals. The multilayer design, i.e., the individual layer thicknesses and the total number of bilayers, directly influences the resultant reflectance and careful determination was therefore made with the aid of computer simulations.

All multilayers were grown on chemically cleaned Si substrates by ion-assisted dual target magnetron sputtering under high vacuum ($\sim 10^{-7}$ Torr) conditions. The effect of low and high ion-flux bombardment of low energy ($< 50$ eV) Ar ions, on growing surfaces was studied for all material systems. Furthermore, a two-stage deposition of each individual layer with modulated ion-energies was applied in order to obtain smooth and abrupt interfaces with as small intermixing as possible. Ion-surface interactions were also theoretically considered for estimating an appropriate ion-flux and ion-energy range desired for sufficient ad-atom mobilities.

X-ray reflectivity and transmission electron microscopy have been the main probes for multilayer characterization in this work. For the Cr/Ti multilayer designed for normal incidence and grown with optimized two-stage ion-energy modulation, a peak reflectance of 2.1% was achieved at the Ti-$2p$ absorption edge ($\lambda = 2.74$ nm). For a multilayer mirror designed for the Brewster angle a maximum reflectance of 4.3% was accomplished. These measurements were made at the synchrotron radiation source BESSY in Berlin. Specular reflectivity and diffuse scattering scans were utilized for quantitative and qualitative analysis of the vertical and lateral structure of the multilayers. At-wavelength measurements of a series of Cr/Ti multilayers revealed the accumulation of roughness with increasing number of bilayers
(\(N > 100\)) for this material system. Hard X-ray reflectivity and diffractometry were used for quality checks of the multilayers for rapid feed-back to the deposition. In-situ annealing using hard X-ray reflectivity was also performed to assess the thermal stability of Cr/Ti multilayers. It was found that probably due to a strong thermal diffusion the degradation of multilayers (with bilayer period of 1.37 nm) in this material system occurs just above the growth temperature (\(\sim 40^\circ C\)). The accumulation of a low spatial frequency “waviness” with increasing number of layers in Cr/Ti multilayers was investigated by transmission electron microscopy. The influence of process conditions on multilayer structure with different periodicities was investigated by TEM analyses of a series of three samples for each of the above-mentioned material system. The Cr/Sc multilayers have shown the most flat and abrupt interface structure without any significant roughness evolution when grown with optimum process parameters.
Preface

An interesting prospect of working in connection with thin films and X-ray optics was the first attraction for continuing this field of research. However, after spending two years in learning multilayer growth and wondering about characterizing, what I have grown? I have realized that it is a rather larger inter-connection of the fields in physics. Whenever I feel unmotivated, a curiosity to interlink one physical aspect with another drives me to work. I believe, finally I would have a little ability to tie the threads at the right corners.

For me it has certainly been a nice experience of staying in all these years at Linköping and working at Thin Film Physics Division. I am thankful to all the people who are part of my life regarding work, fun or just being around to give me the inspiration.

Considering the fact that I was an alien to the field of X-ray multilayer mirrors when I first started, I truly give all the credit to my advisor, Associate Prof. Jens Birch for introducing me to this exciting field. I am inspired by the knowledge he possesses in the field and his enthusiasm for X-ray mirror research. I express my deep sense of gratitude for all knowledge and confidence he has given me and for his patience and kindness that he exhibited towards me. It means a lot to me. Thanks Jens!

I am particularly thankful to Dr. Fredrik Eriksson for his significant contribution in performing experiments, writing papers and having interesting discussions. I really am proud on our friendship. By the way, how you manage to always being around whenever I need you?

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Thin Film Group, you are the ”best” group in the world. Thanks for the cooperation and
lets continue our fun plans!!

Halldora, for providing me a home away from home.

I have always been fortunate to have some of the best and most supportive friends one could ever want. Thanks God for it!! but I really don’t know how to say thanks to them. I am really thankful to:

Anders Elfving, the sports master, thanks for such a nice friendship in all these years.

Uzma & Aeysha, I guess you are the only ones, whom I can be angry with whenever I want.

Anders, Axel, Timo, Johan, Martina and Ming, thanks to all of you for your great company, especially during lunch and coffee hours.

Finally, I extremely appreciate all the support from my family, especially from my Parents, you have always been a great source of strength.

Naureen
Publications

Papers Included in the Thesis:

Paper I
Interface Engineered Ultra-short Period Cr/Ti multilayers as High Reflectance Mirrors and Polarizers for Soft X-rays of $\lambda = 2.74$ nm Wavelength

N. Ghafoor, F. Eriksson, P. O. Å. Persson, F. Schäfers, J. Birch
Applied Optics, Accepted, 2005

Paper II
HRTEM Study of Cr/Sc Multilayers: Effects of Ion-assisted Growth

N. Ghafoor, F. Eriksson, P. O. Ä. Persson, J. Birch
In manuscript, 2005

Paper III
Atomic Scale Interface Engineering by Modulated Ion Assisted Deposition giving Outstanding Soft X-ray Multilayer Mirror Properties

Applied Optics, Submitted, 2005

Other Publications:

Paper IV
Interface Engineering of Short-period Ni/V Multilayer X-ray Mirrors.

F. Eriksson, N. Ghafoor, F. Schäfers, E. M. Gullikson, and J. Birch,
Thin Solid Films, Submitted, 2005

Paper V
Single Crystal CrN/ScN Superlattice Soft X-ray Mirrors: Epitaxial growth, Structure, and Properties

J. Birch, T. Joelsson, F. Eriksson, N. Ghafoor, L. Hultman
Thin Solid Films, Submitted, 2005
Paper VI
Influence of Concurrent Ion-bombardment During Magnetron Sputter Deposition of Mo/Si Multilayers
J. Romero, N. Ghafoor, F. Eriksson, and J. Birch
In manuscript, 2005
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Chapter 1

Introduction

The work presented in this thesis is a continuation of a project on developing soft X-ray multilayer mirrors that has been in progress in the Thin Film Physics Division during the last 5 years. This chapter contains a general introduction to X-ray multilayer mirrors and their increasing interest for fabrication of advanced instrumentation operating in the soft X-ray range. Previous experiences in the research group are summarized together with a motivation for further continuation of the project. The last section contains a brief introduction to the chapters included in the thesis.

A desire to enable X-ray vision and X-ray imaging of nm sized objects has established a rapidly growing field of research, covering all areas from X-ray source development to X-ray imaging and spectroscopy instrumentation. Since 1895, soon after the discovery of X-rays, the advancement in X-ray sources has been a non-stop technology and X-rays which, at that time, were produced in a small vacuum tube are now also generated at large synchrotron radiation facilities with 15 orders of magnitude higher average spectral brightness than their first production. The state-of-the-art is the “X-ray free-electron laser” which is a coherent and highly brilliant X-ray source based on a lasing principle. It is expected to unearth many challenges of scientific research due to its additional provision of femtosecond time-resolved studies. Unfortunately, the instrumentation development for utilizing this high brilliance radiation is lagging.
far behind the source development. Especially when it comes to the collection, collimation 
and convergence of X-rays, for building X-ray microscopes, spectrometers, polarimeters or po-
larizers, X-ray lithography tools required in the electronic industry, X-ray diagnostic of high 
temperature plasma and for exploring the fascinating world of cosmology and astronomy by 
solar imaging instruments or deep space telescopes operating at wavelength of natural X-ray 
sources [1]-[5]. In short, the advanced optical elements needed for realizing the above mentioned 
instrumentation are immature components and need to be further developed.

The spectral region, extending from a wavelength of roughly $\lambda = 0.01$ nm to about 
50 nm, is generally (although the boundaries are diffuse) categorized as hard X-rays (HXR), 
$\lambda < 0.5$ nm, soft X-rays (SXR), $0.5 < \lambda < 10$ nm, and extreme ultraviolet radiation (EUV), 
$10 < \lambda < 50$ nm [6]. EUV radiation is vital for smaller wavelength lithography in the electronic 
industry, while the region of particular interest for the biosciences is ranging from the oxygen 
absorption edge, $\lambda = 2.4$ nm, to the carbon absorption edge, $\lambda = 4.4$ nm called “the water 
window”. Here the X-ray radiation is absorbed by carbon but transmitted through oxygen, 
and this high natural contrast is indeed very attractive for imaging biological specimens in 
their natural aqueous environment [7]-[9]. Although, most of the discussion in this thesis is 
generally true for all X-ray wavelengths, the research presented here is mainly focused on soft 
X-rays for water window microscopy applications.

Conventional optical elements, lenses or thin film coated mirrors are not applicable 
when the interaction radiation is X-rays. This is mainly due to a small refractive index at these 
wavelengths for all materials compared to vacuum which, as a consequence, gives negligible 
refraction. Further, a use of thicker lenses in order to get noticeable refraction, is also obstructed 
by the highly absorbing nature of matter for soft X-rays. An exception to this, is total external 
reflection of X-rays at very low incident angles, which allows to use large sized singly coated 
grazing incident mirrors as converging optics. Nevertheless, from a technological point of view 
normal-incidence optics, for instance, multilayer mirrors, are currently desired as they would 
have many advantages over the grazing ones. Since all X-ray wavelengths are reflected below 
the critical angle, wavelength dispersion with high spectral resolution can only be achieved by 
specifically designed mirrors at higher angles. Mirrors for normal incidence are comparatively 
small and are easier to fabricate with less aberrative defects, as well as with large field size for 
imaging instruments. Ideally, they would have high efficiency due to a large collection area and
1.1. PREVIOUS EXPERIENCE

above all the size of the mirror and radiation collection geometry would enable the possibility to build compact, small sized, laboratory instruments. However, this requires a highly reflective surface which can only be accomplished by multilayer interference coatings \[10\].

Multilayer interference coatings, often referred to as multilayer mirrors, are formed by depositing alternating layers of usually two materials of dissimilar refractive indices that form a long-term stable interface. In multilayer mirrors, reflection occur at each interface due to the discontinuity in the complex refractive index, \( \eta \), of the constituting materials. By tailoring the layer thicknesses, the reflectivity, \( R \), versus wavelength, \( \lambda \), or \( R \) versus grazing incidence angle, \( \theta \), can be designed to follow a curve of any desired shape. For instance, this project has mainly been focused on achieving highest near-normal incidence \( (\theta \approx 90^\circ) \), reflectivity of a particular X-ray wavelength from multilayer mirrors facing line emitting soft X-ray sources.

Today, the major challenge in the multilayer mirror field is to find optically and chemically compatible materials for consecutively growing up to thousands of sub-nm thin layers with abrupt and sharp boundaries. Another challenging area for the multilayer community is the methods of detailed multilayer characterization of buried interfaces. X-ray reflectivity, XRR, being one of the most valuable probes, have extensively been used for deducing mirror performance but it does not explicitly provide complete in and out-of-plane structural information of layer stacks when it comes to 0.3 to 1 nm thin layers with < 0.3 nm interface width. For direct imaging of the multilayer microstructure, transmission electron microscopy, TEM, have successfully been applied for comparatively thicker layers > 2 nm, but again, investigations of the local surroundings of an atom present at an interface is a somewhat complicated task. Moreover, the nucleation and growth methodology of metal multilayers, which is an essence of this thesis, have not been fully understood especially when multilayers are grown under highly non-equilibrium conditions with growth kinetics controlled by ion-assistance. All these matters are, to some extent, addressed in this thesis.

1.1 Previous Experience

An extensive research for better understanding of the growth mechanisms of sub-nm thin multilayer X-ray mirrors has already been initiated by the Thin Film Physics Division at Linköping University. In particular, the main focus has been to develop a large, shaped, 65
mm diameter, normal incidence condenser mirror for a compact SXR microscope located at the Royal Institute of Technology, KTH, in Stockholm. Despite considerable problems in synthesizing a uniformly reflecting mirror in a small deposition chamber, shaped mirrors with an average reflectivity of about 0.5% were accomplished for the desired wavelength (\( \lambda = 3.374 \text{ nm} \)) \([11]\).

In the course of this project, a great deal of knowledge has been gained regarding the growth of extremely thin multilayers. Several different multilayer systems, for example W/B\(_4\)C, Cr/Sc, Ni/V, Ni/Sc and CrN/ScN were thoroughly studied with widespread perspective of material selection, operating wavelengths, angles and growth conditions. Since dual-cathode magnetron sputtering was chosen for growing multilayers, parameters such as the sputtering gas, the ion-flux and the ion-energy were varied and their impact on layer morphology and interface structure was explored for different material systems. The significance of plasma characterization i.e. the determination of plasma potential, relative ratio of containing species (ions and electrons) and ion-to-neutral ratios has been realized early on. In this regard, plasma characterization probes have been manufactured and were routinely used to determine the ion-fluxes and ion-energies prior to deposition of any multilayers with a new material system or with new deposition conditions.

The current research has also been partly dedicated to the analytical calculation of appropriate ion-surface interaction energies in order to get theoretical insight of the ion bombardment impact on otherwise kinetically restricted low temperature growth. Computer simulations at all stages as: material selection, multilayer design, mirror performance, and for detailed interface information have been well established in order to improve the mirror performance \([12]\).

Table 1.1: Some of the previously published results for different multilayer combinations at the Thin Film Physics Division.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \lambda ) (nm)</th>
<th>( \Lambda ) (nm)</th>
<th>N</th>
<th>Normal incidence, ( \theta^o )</th>
<th>Reflectivity, R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr/Sc</td>
<td>3.117</td>
<td>1.59</td>
<td>600</td>
<td>80.5°</td>
<td>20.7</td>
</tr>
<tr>
<td>Ni/V</td>
<td>1.22</td>
<td>1.22</td>
<td>400</td>
<td>88</td>
<td>2.7</td>
</tr>
<tr>
<td>CrN/ScN</td>
<td>3.117</td>
<td>1.74</td>
<td>61</td>
<td>63</td>
<td>6.95</td>
</tr>
</tbody>
</table>

As a consequence of a systematic and detailed understanding of the fundamental physics involved in determining layer structure and interface perfection the highest normal incidence
reflectivity of 14.5% for Cr/Sc layer system at Sc absorption edge, $\lambda = 3.11$ nm, was reported in 2003 [13]. This was a breakthrough in achieving a maximum reflectance both in this energy range and with this material system. Further, improvement in reduced interface roughness was obtained by introducing a novel interface engineering technique using a two-stage, low-energy, high-flux, ion-assisted growth of each individual layer in a multilayer stack. The engineered interfaces contributed to an enhancement in reflectance and a peak reflectivity of 20% was obtained for Cr/Sc multilayers [14]. Absolute reflectivities, for some of the previously tested systems, with corresponding bilayer periods, $\Lambda$, operating angles, wavelengths, and fabrication description are summarized in table 1.1.

### 1.2 Research Inspiration

A profound outlook of the above mentioned innovations in the multilayer field as well as the state-of-the-art obstacles have driven the following multilayer research. The search and growth of new material combinations, especially for wavelength dispersive near-normal multilayer mirrors for line-emission like produced plasma, LPP [9] and Čerenkov radiation [15] based sources, indeed motivated thin multilayer deposition research. Investigation of X-ray reflectivity dependence on layer morphology, local interface environment and overall roughness prevalence for different material systems have been leading incentives during all this time. In parallel to the X-ray reflectivity, a extensive use of cross-sectional transmission electron microscopy of multilayers has also evolved due to the need and interest for nano structural roughness investigations.

### 1.3 Outline of the Thesis

The content of the research is compiled into five chapters in this thesis. The next chapter deals with the general description of X-ray reflection from a multilayer structure and also the most commonly used terminologies in the field are introduced. Material selection and mirror design rules, followed in this work, are also described. Chapter 3 is a detailed outlook of metal multilayer growth related issues. Characterization techniques and interface quality analysis is further described in chapter 4. Chapter 5 includes a summary of the work accomplished until
now, and also draws attention to future research. Some of the results have been compiled into scientific publications and are included in the end of the book.
Chapter 2

Soft X-ray Multilayer Optics

In order to reflect soft X-rays a multilayer should have specific layers materials, arranged in accordance with the reflecting wavelength and the reflecting geometry. No matter how accurate the multilayer has been designed certain imperfections are always present, reducing the reflectivity. The principle of X-ray reflectance from a specially designed multilayer, and some of the related multilayer imperfections in this context are described in this chapter.

2.1 Multilayer Mirrors

Soft X-ray multilayer mirrors are fabricated by sequential layer deposition of materials with a large contrast in X-ray optical properties. The parameters that can be varied in, for instance, a periodic multilayer containing bilayers as illustrated in Fig. 2-1 are the substrate, the two different layer materials, A and B, the order of the layer (ABAB.. or BABA..), the total number of bilayers, N, and finally the individual layer thicknesses, \( d_A \) and \( d_B \). Among the multilayer community, combinations of these parameters like the vertical repetition of the bilayers i.e., multilayer or bilayer period, \( \Lambda = d_A + d_B \), and the multilayer thickness ratio, \( \Gamma = \frac{d_B}{d_A + d_B} \), between the top layer thickness and the period, are the most commonly used expressions for differentiating multilayers. Exceptions to this general design are the deposition of a buffer layer on the substrate for enhanced multilayer adhesion or more commonly the capping layer.
to protect the top of the whole multilayer from oxidation. Also non-periodic multilayers exist for broadband multilayer applications.

2.2 X-ray Reflectivity

An X-ray photon can interact with an atom in many ways: it can be scattered, diffracted, reflected, or absorbed. Scattering is a process by which the incident radiation is redirected over a very wide angular pattern, generally by disordered systems or rough surfaces, while in diffraction incident radiation is redirected into relatively well-defined directions by ordered arrays of scatterers. Bragg’s law [16] explains the condition of diffraction from a regular 3D crystal as,

$$m\lambda = 2\Lambda \sin \theta.$$  \hspace{1cm} (2.1)

where $\Lambda$ is the spatial periodicity, $\lambda$ is the X-ray wavelength, $m$ is an integer called the order of diffraction, and $\theta$ is the angle of X-ray incidence measured from the reflecting plane.

In multilayers, which are one dimensional analogues of 3D crystals, mirror reflection occur at each interface due to the discontinuity in the complex refractive index, $\eta$, of the two
2.2. X-RAY REFLECTIVITY

Figure 2-2: An optical model [17] for X-ray reflection from a multilayer containing N bilayers and n+1 interfaces. X-ray reflections from the substrate, \( n = 0 \), till the vacuum-multilayer interface \( (n+1) \) are shown. A typical reflectivity curve achieved versus the angle \( \theta \), is shown on the top. Peak reflectance corresponds to the angle where there is a constructive interference of most interface reflections.

constituting materials. The structure of a multilayer in the direction normal to the layers can be deduced from a measured reflectivity curve as shown in Fig. 2-2. High reflectivity is obtained by a multilayer when all bilayers in the multilayer are optimized to add reflected X-rays in phase. Reflection of X-rays at interfaces have two basic differences from the case of visible light: the deviation in the index of refraction from unity is tiny, and the refractive index is less than one. In general for X-rays the complex refractive index of a material can be expressed as,

\[
\eta = 1 - \delta + i\beta. \tag{2.2}
\]

To account for the refractive index Bragg’s law is then modified [18] as,
\[ m\lambda = 2\Lambda \sin \theta \sqrt{1 + \frac{(1 - \delta)^2 - 1}{\sin^2 \theta}}, \]  

(2.3)

where \((1 - \delta)\) is the average real part of the refractive index which in the case of bilayers is:

\[ \bar{\delta} = \frac{d_A \delta_A + d_B \delta_B}{d_A + d_B}. \]

(2.4)

\(\delta_A\) and \(\delta_B\) are the dispersion coefficients of the layer A and B respectively. The \(\bar{\delta}\) is on the order of \(10^{-5}\) in solid materials and only around \(10^{-8}\) in air. The imaginary part \(\beta\), which accounts for absorption, is usually very small for HXR but significantly higher for SXR wavelengths. This means that the X-ray wavelength is slightly shorter inside the material than in air or vacuum. For normal incidence, \(\theta = 90^\circ\), Eq. 2.3 will reduce to,

\[ \Lambda = \frac{m\lambda}{2\bar{\delta}}. \]

(2.5)

The above relation implies that the multilayer period \(\Lambda\), which gives constructive interference, is thus slightly smaller than half the X-ray wavelength for the first order reflection \((m = 1)\) at normal incidence.

### 2.3 Material Selection for Soft X-ray Mirrors

A large difference in electron density of a high and low atomic number, \(Z\), between the layer materials provides refractive index contrast and can be useful as a guide for material selection. However, a more detailed study of the optical properties will expand the possibilities. For multilayers discussed in this thesis, the material selection was based on the combined optical properties as a function of wavelength of the multilayer constituents.

In general, optical theory implies that at normal incidence reflectivity, \(R(\theta) = I(\theta)/I_0\), i.e. the fraction of the incident X-ray intensity reflected at normal incidence, \(\theta = 90^\circ\), from ideal single interface is approximately,

\[ R \approx \frac{(\Delta\delta)^2 + (\Delta\beta)^2}{4}, \]

(2.6)

where, \(\Delta\delta\) and \(\Delta\beta\) are the differences in dispersion and extinction coefficients between the two
2.3. MATERIAL SELECTION FOR SOFT X-RAY MIRRORS

Layer-materials, respectively. The coefficients are in turn related to the operating wavelength and the complex atomic scattering factors as,

\[ \delta = \frac{N_a r_e \lambda^2}{2\pi} (f_o + f') \]

and,

\[ \beta = \frac{N_a r_e \lambda^2}{2\pi} f''. \]

Here, \( N_a \) is the atomic density, \( r_e \) is the Thompson scattering length, \( f_o \) is the Thompson scattering factor and \( f' \) and \( f'' \) are the real and imaginary dispersion correction factors to the Thompson scattering factor. The extinction coefficient \( \beta \) can also be defined as,

\[ \beta = \frac{\mu \lambda}{4\pi}, \]

where, \( \mu^{-1} \) accounts for the attenuation of X-rays to a characteristic length of \( 1/e \), in a material and is called absorption coefficient.

Figure 2-3: Periodic table of the elements. Some transition metals and other potential elements for soft X-ray multilayer mirrors are highlighted.

Predominantly, material selection was made for mirrors apt for line-emission sources.
like the LPP or Čerenkov radiation sources. Therefore, the materials having their absorption edges within the water window like transition metals Ti, V and Sc were picked for mirror design. An intention behind choosing these materials was the so called “anomalous dispersion” of X-rays at the corresponding edges where the refractive index becomes slightly more than unity, which in turn, could be utilized to get the enhanced reflectance.

For example, anomalies in $\delta$ and $\beta$ for titanium, at the Ti-2$p$ absorption edge ($\lambda = 2.74$ nm, $E = 452$ eV) are illustrated in Fig. 2-4 (a). In order to select the second layer material with Ti the optical constants, $\delta$ and $\beta$, for several other elements were plotted in the same graph for $\lambda = 2.74$ nm, see Fig. 2-4 (b), and Eq. 2.6 was partially used to pick few materials which have given maximum difference in $\Delta \delta$ with Ti. The mentioned condition, $\Delta \beta$ to be maximum does not entirely hold true when combined reflections from a large number of interfaces are desired. In that case a large $\beta$ will lead to significant absorption of penetrated X-rays according to Eq. 2.9 and only reflection of a few top interfaces will contribute to the reflected intensity. Hence, the maximum $\Delta \beta$ selection rule was relaxed and the second materials were also selected from the low $\beta$ region and the probability of higher reflectance was then increased by designing mirrors with a large number of interfaces $\sim 200 - 300$.

![Figure 2-4: (a) Discontinuities in Ti optical constants, $\delta$, and $\beta$, at 2$p$ absorption edge. The values of $\delta$ are negative close to an absorption edge which made the $\eta$ to be slightly more than unity. (b) 2D- $\delta \beta$ plot for variety of high refractive index materials, than Ti, at Ti-2$p$ edge.](image)

As shown in Fig. 2-4(b), there are a few materials, in the lower right corner from
2.3. MATERIAL SELECTION FOR SOFT X-RAY MIRRORS

Figure 2-5: Reflectivity vs. number of bilayers simulations for Cr and Ni, as counter part of Ti based multilayer systems. The effect of higher $\beta$ of Ni becomes dominant for $N > 300$.

$\delta > 0.003$, which fulfilled the above criterion of selection, however strongly magnetic materials like Fe and Co were discarded due to expected difficulties in deposition processes and the remaining Ni, Zn, Mn, and Cr were simulated with Ti for maximum reflectance for a semi infinite multilayer at normal incidence. Cr/Ti has, compared to other material combinations, given a maximum theoretical reflectivity of $\sim 46\%$, and was therefore selected for experimental tests. Simulations also suggested Ni/Ti as an alternative or an even better combination, if fewer number of bilayers are sufficient to accomplish the mirror application. As evident from the simulated reflectivities in Fig. 2-5 Ni/Ti would have given higher reflectance up to about $N > 300$ bilayers (because of the higher contrast in $\delta$) thereafter it saturates while Cr/Ti allows more than 300 bilayers to contribute to the reflectivity, and hence the reflectivity increases beyond $N = 335$, due to the lower overall absorption [19]. In this particular case, the material selection was based on the research interest of studying multilayer systems with a large number of interfaces and to obtain maximum achievable reflectivity.

Occasionally, it has also been shown for EUV and soft X-ray mirrors that physical and especially chemical considerations of materials properties are absolutely essential for structural improvement of interfaces in multilayers. For example, the tendency of miscibility, chemical diffusion or reactions of the selected material combinations, occurring across the material boundaries, may deteriorate the interface structure and hence the resultant reflectance. Few
materials like Si, C, B, and B$_4$C, are known for their smooth and amorphous growth and have been used as a counterpart of metal multilayer systems, like for example C/Ti and the famous Mo/Si system or as diffusion barriers between optically selected metal layers. For Cr/Ti multilayers (selected according to the above criterion), a maximum near-normal incidence peak reflectance of 2.1% at $\lambda = 2.74$ nm have already been achieved [20]. However, to compare with other possibilities, simulations are performed in Fig. 2-6 (a), incorporating B$_4$C as an additional material. The optical properties of the relevant materials are also shown Fig. 2-6 (b).

For all three multilayer structures the same $\Lambda$ and equal $\Gamma$ of the two major constituents were considered. Simulations were made for 300 bilayers assuming absolutely abrupt and sharp interfaces. As can be seen, a pure Cr/Ti metal combination have clearly the maximum theoretical reflectance, thereafter the reflectivity is reduced for B$_4$C/Ti. Even lower reflectivity is obtained when a 0.19 nm B$_4$C layer was introduced in-between the Ti and Cr layers. Coming back to the selection criterion, optical constants particularly large $\beta$'s or large photoabsorption cross-sections, $\mu$, for B$_4$C explain the low reflectivity when combined with Ti in one or another way. However, a 5% reflectivity reported for C/Ti multilayers [21], and recently achieved remarkable reflectance of 17% for a Cr/B$_4$C/Ti/B$_4$C layered structure [14], at the Ti-2p absorption edge have revolutionized the optical standards of material choice. A closer approach to theoretical reflectance, by incorporating these materials, undoubtedly assures the presence of abrupt and sharp interfaces. The structural influence of different materials at the interface will again be discussed in the context of roughness evolution in chapter 4.

2.4 Multilayer Design

Design of, for example, a periodic multilayer means the determination of the multilayer period, $\Lambda$, the layer thickness ratio, $\Gamma$, and the total number of bilayers, $N$. By using the IMD [22] software, which is a computer program for modelling the optical properties of multilayer films, the combination of $\Lambda$ and $\Gamma$ giving the highest reflectance can be found. Required input parameters for such simulations were the selected elements with known optical constants (including substrate material), the order of materials, the operating wavelength, and the incidence angle. The order of materials, which in turn determines $\Gamma$, should be chosen to obtain highest optical contrast between vacuum ($\eta_0 = 1$) and the top layer material, to achieve maximum
2.4. MULTILAYER DESIGN

Figure 2-6: (a) Comparison of normal-incidence theoretical reflectance of three multilayers calculated at $\lambda = 2.74 \text{ nm}$ ($E = 452 \text{ eV}$). (b) Optical constants of simulated materials.

reflectance according to Eq. 2.6. However chemical reactivity of the materials also needs to be taken into account and sometimes a capping layer might be needed. In the Cr/Ti system, Cr is chosen as the top layer because of its ability to form a passive oxide layer over the highly reactive Ti.

Once $\Lambda$ and $\Gamma$ are known for a multilayer system the next step in designing is the determination of the total number of bilayers to obtain maximum achievable theoretical reflectance. Since, the reflectivity from a single interface (Eq. 2.6) is typically on the order of $10^{-4} - 10^{-6}$ at near-normal incidence, therefore, in-phase reflections from $10^2 - 10^3$ interfaces are required to add in order to reach a maximum, thereafter, absorption in the multilayer stack limits the reflectivity. Again, simulations can be performed to obtain $N$ corresponding to saturation reflectance. A maximum reflectance by no means is the only requirement to determine $N$. Wavelength dispersive multilayer mirrors act as narrow-band pass filters and need as high reflectance as possible at a single wavelength, while broad-band pass filters are normally designed to reflect large range of wavelengths with uniform reflectivity. The selection rule for estimating the effective number of bilayers with respect to the spectral resolving power is,

$$\frac{\Delta \lambda}{\lambda} \approx \frac{1}{mN}. \quad (2.10)$$
2.5 Real Interfaces and Associated Roughness

Until now, it has been assumed that each interface in a multilayer is chemically abrupt and atomically flat without any irregularities. By definition, such an interface is known as an “ideal interface” and physically would be the one having an infinitely small width of the interface. However, in reality, such interfaces never exist. Several phenomena like thermal diffusion, intermixing, atomic irregularities, impurities incorporation, structural transitions, induced stresses etc., result into a finite width of the real interface. Whatever the phenomenon is, an increase in the interface roughness drastically deteriorates the reflectivity of a multilayer. The word “roughness”, frequently used for uneven surfaces, has multifaceted interpretation when it is linked with an interface and gets even further complicated when it is interpreted for several consecutive interfaces in a multilayer system.

The simplest way of defining the roughness at an interface is to consider whether the transition of refractive index is abrupt, continuous, step-like or a combination of these functions at the boundary of the two materials. This in turn, gives rise to an interface profile function, \( g(z) \), usually defined as the normalized average of the refractive index along the growth direction, \( z \), \[23\] and mathematically represented as, \( g(z) \to 1, z \to \infty \). The spatial derivative of the profile function is;

\[
f(z) = \frac{g(z)}{dz}, \tag{2.11}
\]

A more common notion for a transition region is an “interface width, \( 2\sigma \),” which, is an average amplitude of surface height fluctuations and related to the interface profile as;

\[
\sigma = \int z^2 f(z) dz \tag{2.12}
\]

Most generally, the deviation from an ideal interface is categorized in an intermixed (chemically diffuse) and rough (physically distorted) interface. The \( \sigma \) for three types of multilayers, i.e. for ideal, intermixed and rough interfaces is shown in Fig. 2-7 along with the corresponding profile functions. For an ideal interface, \( g(z) \) is a unit step function characterizing infinitesimally thin interface widths, \( \sigma = 0 \), while for the intermixed interfaces, the refractive index varies smoothly in the \( z \)-direction and therefore \( g(z) \) traced the compositional
2.5. REAL INTERFACES AND ASSOCIATED ROUGHNESS

Figure 2-7: One dimensional interface profile function \( g(z) \) and its spatial derivative \( f(z) \) for ideal, intermixed and rough interfaces. The later two kinds have the same interface width \( \sigma \).

For rough interfaces there are discontinuous changes in refractive index at the interface boundaries and \( g(z) \) is accounted by normalizing height distributions. The averaging aspect of the “interface width” concept is clear from the figure, where two different interface structures i.e. a chemically intermixed and a physically rough interface resulted in an identical \( g(z) \), \( f(z) \), and hence also similar \( \sigma \). An obvious disadvantage of using this formalism for roughness analysis is therefore, the lack of discrimination of one kind of roughness over another for complex interface structures constituting mixed profiles.

In most cases, the overall shape of the deviation from an ideal interface is taken into account as a Gaussian distribution and is expressed as a “Debye-Waller” factor which incorporates average interface width as “r.m.s roughness, \( \sigma \),” into the multilayer reflectivity theory as;

\[
R = R_o e^{-\left(\frac{4\pi \sigma \sin \theta}{m \lambda}\right)^2}
\]  

(2.13)

where,

- \( R \) = absolute reflectivity
- \( R_o \) = theoretical reflectance for an ideal interface
- \( \sigma \) = average interface width
- \( \theta \) = grazing incidence angle
\( \lambda \) = X-ray wavelength

\( m \) = order of Bragg reflection

The exponential dependence of absolute reflectivity, \( R \), on \( \sigma^2 \) for a single interface is clearly more dominant for shorter soft X-ray wavelengths or shorter multilayer periods (Eq. 2.1) and/or higher incidence angles. An enhanced impact of increasing interface width on shorter X-ray wavelength can be seen in Fig. 2-8 (a), where the normal incidence reflectivity is simulated versus the interface width at three wavelengths (\( \lambda = 13.4, 3.11, 2.74 \) nm) for three multilayers, each containing \( N = 1000 \) periods, suitable at corresponding wavelengths. On the other hand simulations performed on the shortest \( \lambda \), i.e. for a Cr/Ti multilayer explains, Fig. 2-8 (b), the angular dependence of radiation geometry on the interface width. At normal incidence the reflectivity is decreased to 30% of the maximum on adding only 0.3 nm interface width, while at 45° incidence it reduced to 66% of the initial value. In short, both shorter wavelength and higher angle X-ray reflections require multilayers with extremely small periods and in order to have minimum ratio of \( \sigma/\Lambda \) (Eq. 2.13) the interface width, \( \sigma \), if not completely eliminated, should be as small as possible.

![Figure 2-8](image)

Figure 2-8: (a) Normal-incidence reflectivity simulations versus the interface width for three different wavelengths (designed with appropriate bilayer periods). Multilayer materials at each wavelength are chosen according to the above described criterion. (b) Reflectivity dependence simulations on interface width at normal incidence, \( \theta = 90^\circ \), and at \( \theta = 45^\circ \), for a Cr/Ti multilayer at \( \lambda = 2.74 \) nm.
2.5. **REAL INTERFACES AND ASSOCIATED ROUGHNESS**

Figure 2-9: (a) High, (b) low, and (c) mixed spatial frequency roughnesses for single interfaces, all having similar average interface height fluctuations of $2\sigma$. $\xi_q$ indicates the lateral coherence length, while $\alpha$ measures short range disorder within $\xi_q$. (d) $\xi_\perp$ is a measure of the vertical correlation length for a multilayer.

The surface height fluctuations, if not completely uncorrelated, can be further classified on the basis of lateral, $\xi_q$, and vertical, $\xi_\perp$, roughness parameters called correlation lengths. These are the characteristic length scales: between lateral repetition of roughness features, and vertical extent up to which roughness reproduce its initial occurrence. As shown in the Fig. 2-9 for a single interface, a surfaces associated with a shorter $\xi_q$ (compared to the X-ray wavelength) will be more “jagged” (a), while longer $\xi_q$ (also termed as low spatial frequency roughness) correspond to locally smooth but “wavy” surfaces (b). A combination of these two (c) actually needs an extra parameter, $\alpha$, which provides a measure of short range ($< \xi_q$) surface roughness embedded in $\xi_q$.

Associated with a multilayer having many consecutive interfaces, are other kinds of roughnesses. As already described the roughness progression correlated perpendicular to the interfaces is described by $\xi_\perp$. For almost all multilayer systems the overall roughnesses are increasing with increasing number of bilayers or the total thickness of the stack. One consideration is the increment in roughness at each new interface, due to limited ad-atom mobility on the surfaces, built in growth stresses or properties intrinsic of materials, which build up an accumulating roughness.

From the multilayer X-ray reflectivity point of view the lateral roughness correlation will
increase the diffusely scattered intensity around the specular beam, and the correlation length will effect the angular distribution of the incoherent halo around the specular direction. On the other hand, vertically correlated roughness will behave like an ordered structure and reflectivity will distribute into sheats where the Bragg condition is fulfilled. Accumulated roughness effects can also be recorded as diffusely scattered intensity around reflectivity peaks [24], [25], [26]. One should keep in mind during roughness interpretation that the reflective features of a multilayer with correlated interfacial roughness change non-linearly with the operating wavelengths of the mirror and the correlation length scales are all relative.

A quantitative evaluation of the roughness parameters requires an extensive theoretical research and has therefore only been qualitatively studied so far during this work. Varying roughnesses associated with different material systems, used in this work are discussed in chapter 4.
Chapter 3

Multilayer Growth

Theoretical and experimental aspects of sub-nm multilayer growth under the influence of low-energy ion-bombardment are treated in this chapter. Prospects of interface quality improvement and microstructure alteration by ion-assistance are also discussed.

It has been known for a while now that during sputtering, the presence of low-energy ions (25 to 100 eV) impinging on the growing surface facilitate the control of multilayer growth kinetics where layers with low defects densities and smooth interfaces can be realized [27], [28]. Fundamental energetic species involved in sputtering of atoms from a solid target by energetic ion bombardment are schematically shown in Fig. 3-1. The number of atoms removed and the secondary electrons emitted per incident ion are expressed as the sputtering yield, $S$, and the secondary electron yield, $\gamma$, respectively. Both quantities are dependent on the nature of the target material and the bombarding species which, in most cases, are sputtering gas ions from the surrounding plasma. Sputtered atoms are ejected in knock-on collisions and form a film upon condensation on any available surface, for instance a substrate. The energies of the atoms arriving the substrate are normally a few eV, and are insufficient to provide enough surface mobilities to the growing layers. Fortunately, the surface mobility can be enhanced if positive ions from the working gas, extracted from the plasma, are accelerated towards the surface of the growing film, where the growth kinetics and microstructures are influenced by the ion-film collisions. A confinement of secondary electrons by magnetic fields close to the magnetron,
enhances the ionization and hence the sputtering probability. Magnetic fields also provide a way of guiding the ions to the growing surfaces. Sputtering gas neutrals reflected from the target surface is another dominant energetic species. Their energies depend on e.g. the relative masses of the target and sputtering gas atoms and the incoming ion energies. These neutrals can be used as an alternative for ion-bomardment, especially, where magnetic confinement or ion guidance can not be achieved. Before going into the details of experiments and physical aspects of multilayer formation a theoretical model to calculate the required range of ion energies and fluxes for multilayer growth is presented in the next section.

3.1 Theoretical Considerations of Ion-surface Interactions

Several elastic and inelastic processes are involved in momentum-energy transfer, during ion-bombardment of the growing surfaces through nuclear and/or electronic interactions. One of the physical processes where ions transfer their energies is kinetic displacements of the surface or bulk atoms of the growing layers. An estimation of the ion-energy range required to cause surface atom displacements, in order to provide sufficient ad-atom surface mobility while avoiding bulk damage, can be useful in selecting process conditions for soft X-ray multilayer mirrors. For such calculations, the input parameters are energy of the bombarding ions, $E$, surface, $E_{d}^{(s)}$
3.1. THEORETICAL CONSIDERATIONS OF ION-SURFACE INTERACTIONS

Figure 3-2: Surface and bulk displacements energy profile for Ti and Cr lattices.

and bulk \(E_d^{(b)}\) displacement energies of the underlying film, masses of the ion and surface atoms and angles of impact. Considering these, a theoretical model based on a binary collision approximation [11] is used to estimate the appropriate ion-energy range prior to multilayer deposition with any new material combination. In the calculations it is assumed that: the cohesive energy of the underlying lattice (closed pack structure) is a direct measure of the bulk displacement energy, \(E_d^{(b)}\) and, owing to fewer chemical bonds and hence weaker bonding strengths the surface displacement energies are assumed to be half of the bulk displacement energies i.e. \(E_d^{(s)} = 0.5E_d^{(b)}\).

Though a simplified approach, in several cases this model has given consistent results with experimental investigations [29]. For example, the deposited energy per ion to cause lattice (surface/bulk) displacements by Ar ion impingement on the growing surfaces of Ti and Cr are calculated versus the initial ion energy from 0 – 100 eV. As shown in Fig. 3-2 at very low ion energies < 21 eV no surface displacements are expected, while ion energies between about 21 eV to 51 eV are more likely to cause displacements ‘primarily’ on the surface or about a monolayer(ML) below the surface layer. Ion energies higher than 51 eV would cause
both surface and bulk (> 1 ML) displacements for this material system. A validation of this calculated energy range, 20 eV to 51 eV, the so called allowed energy-window, has practically been tested [20]. The ion-energy optimization of the Cr/Ti multilayer system, described in a later section, resulted in 21.2 eV and 23.7 eV for Cr and Ti, respectively, which are energies just into the surface displacement region.

An other outcome of the calculations are the required ion-fluxes to cause surface displacements within the energy window. The two horizontal lines in Fig. 3-2 at 13.42 and 11.27 eV indicate $E_d^{(s)}$ of Ti and Cr lattices, respectively. An ion with initial energy of 25 eV will impart a fraction of about 2 eV to lattice displacements, therefore a relatively large number of ions i.e. a high ion-to-metal flux ratio, $\Phi \sim 6$ is needed to assist growth of Cr/Ti multilayers at these low energies.

3.2 Experimental Details

A dual-cathode DC magnetron sputter deposition system with a chamber size of 500 mm diameter, 350 mm in height, and a target-to-substrate distance of 120 mm has been used to deposit all multilayers [30], [31]. The system is equipped with two circular magnetron sources having unbalanced type-II magnetic configuration with opposite polarities. As shown in Fig. 3-3 the two magnetrons, of 75 mm diameter, are mounted at off-axis positions with a tilt angle of 25° to the substrate normal. An electrically isolated µ-metal shield between the magnetrons serves to protect the targets from cross-contamination, and also to push the magnetic field lines closer towards the substrate. This configuration leads to strong magnetic fields from the outer poles extending into the chamber where they couple to a separate solenoid surrounding the substrate. The solenoid consists of 220 turns of capton insulated Cu wire ($\phi = 2$ mm) wound on a stainless-steel frame with an inner diameter of 125 mm. The target materials used were 99.9% pure in all cases and the target discharges were established with constant-current power supplies and discharge currents (voltages) of about 0.06 A (~300 V) were used. This yielded deposition rates of about 0.03 nm/s. Both magnetrons were running continuously during the deposition. The material fluxes to the substrate were regulated by fast acting computer controlled shutters located in front of the magnetrons. All depositions for the current work were carried out using chemically cleaned Si(001) substrates ($40 \times 20 \times 0.5$ mm$^3$) mounted on the electrically isolated
3.2. EXPERIMENTAL DETAILS

substrate table, rotating with a constant rate of 60 rpm. A negative potential of $0 - 50 \text{ V}$ was applied to the substrates during the depositions. The background pressure prior to deposition was about $2 \times 10^{-7} \text{ Torr}$ and a low pressure of about $3 \text{ mTorr Ar (99.999\% purity)}$ gas was maintained during the depositions. The deposition rate of each material was determined by growing two multilayers with known deposition times, but with different layer thickness ratios, $\Gamma$. The multilayer periods were then calculated from the positions of the multilayer peaks in low-angle hard X-ray reflectivity patterns. This yield an equation system from which the individual deposition rates can be extracted [32].

Figure 3-3: An overview of the deposition chamber: Marked components are the magnetrons (1,2), the fast acting shutters (3,4), the isolation shield between the magnetrons (5), the rotating substrate holder (6) and the solenoid (7) surrounding the substrate table.

A solenoid current of either 0 A or 5 A (with a direction that couples the magnetic
field of the solenoid to that of the magnetron being used for deposition), was used to obtain two different field line configurations, shown in Fig. 3-4. The magnetron-solenoid coupling configure the magnetic field lines and can indirectly be seen by the plasma glow (due to ion-electron recombination in high ionization regions) inside the chamber. Fig. 3-4 (a) depicts a situation where the solenoid is turned off (0 A) and the ionization takes place predominantly near to the targets, leading to $\Phi < 1$ at the substrate. Turning on the current (5 A) in an appropriate direction couples the solenoid to either the left Fig. 3-4 (b) or the right Fig. 3-4 (c) magnetron. It can be concluded by ocular inspection of the plasma paths that magnetic field lines guide the secondary electrons (generated in the sputtering process) from the magnetrons all the way down to the substrate where they significantly enhance the ionization of the working gas $(\Phi > 1)$ in the vicinity of the growing film. This enhanced ion-density, as explained earlier, play a central role in providing the required surface energy in order to engineer smooth and abrupt interfaces between growing layers. The applied negative bias to the substrate is used to attract this high flux of ions from the surrounding plasma to the growing film with definite kinetic energies. Absolute values of the ion-energies and ion-to-metal flux ratios, $\Phi$, were determined by plasma probe measurements.

Figure 3-4: Three magnetic field configurations generated by magnetron-solenoid coupling: (a) without a solenoid, (b) left magnetron is coupled with the current in the solenoid and (c) right magnetron is coupled with the opposite current in the solenoid.
3.2. EXPERIMENTAL DETAILS

3.2.1 Plasma Characteristics

The plasma under discussion is a low pressure non-equilibrium discharge, having a low degree of ionization of $10^{-2}$, and the charged particle density i.e. electron density ($n_e$) $\approx$ ion density ($n_i$) of about $10^{-9}$ cm$^{-3}$. In spite of the equivalent charge densities, electrons mobilities being at least 100 times higher than ions normally give the plasma a small positive potential, $V_p$. Another consequence of high electron velocities is the formation of a charge depleted region a so-called “dark space”, close to any surface facing the plasma. For a typical magnetron plasma at low pressure < 10 mTorr, and substrate bias voltages, $V_s$, down to 150 V the thickness of the dark space is on the order of mm. As previously mentioned, the ion energy, $E_{ion}$, and the ion-to-metal atom flux-ratio $J_{ion}/J_{met}$, are the prime measures of how much the growing film can be affected. In order to relate $V_s$ to $E_{ion}$, it is necessary to know the potential of the plasma, $V_p$, at the so called dark space edge, from where the ions are accelerated towards substrate. If the pressure is sufficiently low such that the mean-free path for ions is longer than the dark space, then $E_{ion}$ can be expressed as,

$$E_{ion} = nq | V_s - V_p |,$$  \hspace{1cm} (3.1)

where $n$ is the valency, and $q$ is the charge of the ion. All these parameters depend on the geometry, chemistry and electromagnetic field configuration in the discharge. For most metal targets $E_{ion}$ vary from 0 to 50 eV in this work. In order to characterize the sputtering plasma, I-V curves (Fig. 3-5) measured by electrical probes, placed at the sample position, were used. In such measurements the total probe current, $I_{pr}$, is measured versus the total applied probe voltage, $V_{pr}$ [33].

$I_{pr}$ is the sum of electron and ion-currents, $I_e$ and $I_{ion}$ respectively. The potential where the electronic and ionic contribution to $I_{pr}$ are equal (i.e. $I_{pr} = 0$) is called the floating potential $V_f$ which is the potential attained by the electrically isolated sample. A typical plasma probe I-V curve, as shown in the Fig. 3-5, has three different regions on the basis of $V_p$ and $V_f$.

A. Region A is the ion-saturation region where electrons are repelled by the probe. To determine the ion current density a flat probe of stainless-steel is used. The probe is surrounded by a stainless-steel shield with the same potential as the probe in order to prevent edge effects to influence the effective collecting probe area.
B. In the transition region B, an ion current is collected by the probe and electrons with kinetic energy larger than \((V_{pr}-V_p)\) also reach the probe and contribute to \(I_{pr}\). A *Langmuir probe*, a few mm long tungsten wire, is used to determine the plasma potential in this region, as well as in region A. The plasma potential can be determined by plotting \(\log(I_{pr})\) versus \(V_{pr}\) by the crossings of the tangents of the slopes in the transition region B and in the electron saturation region A, see Fig. 3-5.

C. It is the electron-current region, where the probe potential is higher than \(V_p\), therefore, ions are repelled by the probe and \(I_{pr}\) is governed by \(I_e\).

An Ar sputtering pressure of about \(\sim 3\) mTorr implies about an order of magnitude longer mean free path for ions than the dark sheath. Hence, the probability of collision in the dark space is very low and, for decreasing voltages to the probe no electrons reach the probe, only positive ions are collected. The measured current, \(I_{ion}\), can be used to calculate the ion flux \(J_{ion}\), i.e. the ion current drawn through the sample divided by \(e\) and \(A\) (the area of the probe) according to:

\[
J_{ion} = \frac{N_{ion}}{At}.
\]
Using the deposition rate, $r$, the density of the film, $\rho$, and the molar mass, $M$, of the metal atoms, the flux of metal atoms, $J_{\text{met}}$, can be determined by,

$$J_{\text{met}} = \frac{N_{\text{met}}}{At} = \frac{\rho N_A r}{M}. \tag{3.3}$$

By these two equations, the ion-to-metal flux ratio, $\Phi$, can be calculated as,

$$\Phi = \frac{J_{\text{ion}}}{J_{\text{met}}} = \frac{I_{\text{ion}} M}{\rho N_A r A e}. \tag{3.4}$$

### 3.3 Interface Engineering by Ion-energy Modulation

As compared to a low flux, high ion energy bombardment the use of high-flux bombardment with low energy ions results in homogeneous multilayers with considerably more flat interfaces, as speculated. Nevertheless, the energy of the ions for surface displacement is chosen at the cost of some surface damage which leads to intermixing at the boundaries of two materials for these sub-nm scaled multilayer’s interfaces. In order to get improvement at this point, the research has been further elaborated by the idea of using a two-stage growth mode of each individual layer, so called “modulated ion-assistance”, in order to obtain flat and chemically abrupt interfaces. Theoretically, the concept has been shown to be promising by molecular dynamics simulations for two-stage low-energy ion assistance growth of, Ni/Cu/Ni layers [34].

A growth optimization of Cr/Ti multilayer system is taken as an example here to elaborate the modulated ion-assistance. The plasma potentials, determined from the Langmuir probe measurements, for deposition of these two materials were $V_p(\text{Ti}) = 1.7$ V and $V_p(\text{Cr}) = -1.3$ V, respectively. The negative plasma potential for Cr could be a result of high flux of secondary electrons magnetically guided from the Cr target. The ion-to-neutral flux ratios were calculated to $\Phi_{\text{Ti}} = 3.3$ and $\Phi_{\text{Cr}} = 2.2$, respectively.

The ion-potential (energies) involved at each stage of Ti and Cr layer growth are shown in the Fig. 3-6. The first 0.3 nm of each Ti and Cr layer was grown without ion assistance or technically the substrate was held at 0 V resulting (Eq. 3.1) in $E_{\text{ion}}(\text{Ti}) = 1.7$ eV, and $E_{\text{elec.}}(\text{Cr}) = 1.3$ eV. Practically, these low ion and electron energies have insignificant impact on the growth kinetics and at room temperature deposited atoms will stick on the surface without any displacements. The resulting layer will then be porous and rough, but the probability of
interdiffusion with the underlying layer is expected to be minimal. The remaining 0.39 - 0.72 nm layer thicknesses were then grown with relatively high ion energy (E_{Ti} = 23.7 eV and E_{Cr} = 21.2 eV), which are in the range of calculated energy window for sufficient surface displacements (Fig. 3-2). The intention of increasing the ion energies were to densify the layers and smoothly terminate the surfaces before the onset of the next layer in a multilayer sequence.

Though an indirect way of assessment, experimental success of increased interface quality by modulated ion-assistance is evident from Fig. 3-7, where the first order Bragg peaks in hard X-ray reflectivity scans are compared for three different Cr/Ti multilayers, each containing 20 bilayers. Fig. 3-7 (a), contains the reflectivity curves for the multilayers grown with a continuous ion assistance. The multilayer grown under kinetically restricted conditions with very low E_{ion} = 1.5 eV shows a much reflectance than the multilayer grown with energetic ion-bomardment of E_{ion} = 22 eV. Further, the multilayer grown by ion-energy modulation according to optimized parameters (Fig. 3-6), is compared in Fig. 3-7 (b), and a significant increase in reflectance is obtained. A more direct proof of film and interface quality improvement is illustrated by TEM images in Fig. 3-8 for the above mentioned Cr/Ti multilayers (each containing two multilayer stacks with periods of 1.4 and 2.8 nm). The appearance of denser layers and
3.4 MULTILAYER FORMATION DURING LOW-ENERGY ION BOMBARDMENT

Figure 3-7: Hard X-ray reflectivity scans around the first order Bragg peak for three multilayers each with N= 20. (a) Multilayers grown with continuous ion-assistance, (b) comparison between best obtained multilayer with continuous ion-assistance and modulated ion-assistance.

more distinct and sharper interfaces for continuous and modulated ion-assistances can directly be noticed in comparison with the multilayers grown without ion-assistance. The smoothening or roughness reduction effect of ion-energy modulation seen in these TEM micrographs is a probable explanation for the increase in X-ray reflectivity.

3.4 Multilayer Formation During Low-energy Ion Bombardment

In general, film growth under highly non-equilibrium processes like sputtering is a combined effect of adsorption and diffusion of energetic species as they condense from the vapor phase onto a cold substrate. The number of sputtered species sticking to the substrate are depending on the substrate temperature, deposition rates, impurity concentrations, and involved surface energies. Further, formation of several hundred bilayers in a single multilayer stack with a high interface density is, in addition, greatly influenced by the ion bombardment and layer design.

Unfortunately, the exact spatial and temporal distribution of surface atoms during metal multilayer growth, concurrent with energy transfer by ion bombardment, is not a well-understood area. However a few general “rules” can be spelled out. A dense structure of sub-
Figure 3-8: TEM images of Cr/Ti multilayers grown with different ion assistances where each multilayer contains two stacks: bottom with $\Lambda = 1.4$ nm, and top with $\Lambda = 2.8$ nm. (a) low ion-to-metal flux ratios $< 0.1$ and no ion energy, (b) high-flux ratios $> 2$, and continuous ion-energy of 22 eV and, (c) high-flux ratios with two-stage ion-energy assistance.
3.4. MULTILAYER FORMATION DURING LOW-ENERGY ION BOMBARDMENT

Figure 3-9: A grayscale TEM image of Mo (dark) and Si (light) multilayers with modulated period of, \( \Lambda = 6.9 \) nm. Dark regions inside the Mo layers are diffraction contrast of crystallites. Light gray areas dominant at Si-Mo interfaces are due to silicide formation.

nm thick multilayers with perfectly smooth and abrupt interfaces cannot include crystallites due to the surface roughness associated with a polycrystalline surface. Layer morphology of materials buried inside the interfaces directly influence the interface structure. For example, the classical choice for EUV lithography applications, a Mo/Si multilayer, grown by modulated ion assistance, have resulted into amorphous Si and polycrystalline Mo as shown in the micrograph, Fig. 3-9. A roughness (excluding the intermixing or silicide formation) at Mo-Si interface is an attribute of polycrystalline Mo [35]. The key, for getting smooth surfaces in this case is the densification of Mo layers, for instance, by energetic ion-bombardment, into larger crystallites. It is worth mentioning here that the Mo crystallization into larger grains would also have a positive effect on the reduction of silicide formation, i.e. there will be less interdiffusion of the two materials and one could achieve more abrupt interfaces. In contrast, smoothness and abruptness at interfaces can also be attained by growing amorphous layers of less solubility materials with a positive heat of mixing like Cr/Sc with \( \Delta H = +1 \) kJ/g. Hence, it can be concluded that the layers in a good multilayer should either be epitaxial (so called superlattices) or purely amorphous. Though, beyond the scope of this thesis, it should conceptually be cleared at this point that the “ideal” soft X-ray mirrors, are single crystal superlattices. However, the fabrication of superlattice X-ray mirrors is a somewhat challenging task due to many reasons [36], [37] and therefore amorphous multilayers are desired.
Figure 3-10: Schematic presentation of the three growth modes during the initial stage of layer formation, (a) Volmer-Weber’s island formation, (b) Frank-van der Merwe’s layer-by-layer growth and, (c) a combination of the first two modes is Stranski-Krastanov’s layer plus island growth.

Growth, in general is thought of as one of three ways (Fig. 3-10) of assembling the atoms onto a substrate. The three film formations schematically shown in the figure are traditionally known as (a) Volmer-Weber’s island growth mode, (b) Frank-van der Merwe’s layer-by-layer growth mode and (c) Stranski-Krastanov’s layer plus island growth mode. The parameters $\gamma_A$, $\gamma_B$, are the film and substrate surface energies, respectively, and $\gamma^*$ is the film-substrate interface energy.

The contact angle, $\varphi$, is determined by the growth process and the relations of the surface/interface energies as:

- $\gamma_B < \gamma_A + \gamma^*$ gives $\varphi > 0$ (island growth)
- $\gamma_B > \gamma_A + \gamma^*$ gives $\varphi \approx 0$ (layer-by-layer growth)

It is usually considered in the optical community that growth of metal-on-metal or metal-on-semiconductor begins either by direct island formation or establish into islands after few monolayers i.e. Stranski-Krastanov’s growth mode. This is mainly due to the stronger interactions inbetween the metal atoms than the film-substrate interaction [38], [39]. The growth initiates with 3D island formation which turns into a continuos film upon coalescence of these islands at some threshold thickness. The mean threshold thicknesses are, normally, 1-20 nm for most metals. In practice, fabrication of normal-incidence soft X-ray mirrors demand individual layer thicknesses normally not more than 2 nm and thus island growth would result into a low density, porous, films. Moreover, in multilayers atoms arrange themselves on one (similar) or another (dissimilar) material in short sequences which cannot be compared by single metal film grown on a substrate. The high density of interfaces actually change the layer
morphology by acting as diffusion and dislocation barriers.

Again, one way of visualizing the amorphous growth of the metal-multilayers is thinking of liquid-layers freezing out on to a cold substrate. In order to realize such a formation for extremely thin multilayers the ion bombardment, with appropriate ion-energies during sputtering, is indispensable for structuring metal multilayers as it can:

- Continuously dissociate the formation of nucleated islands, if there are any, and hence favor the rapid quenching of ad-atoms into 2D layers. As a consequence, porosity can be overcome in thin layers and technically it is possible to grow complete layers as this as 0.3 nm.

- Transfer sufficient energy to enhance surface mobility and ad-atom diffusivity in order to trigger the atomic arrangement into smooth layers. This, in addition of layer densification, terminate the surfaces without any irregularities and hence smooth interfaces can be realized.

Figure 3-11: Molecular dynamics simulations done by Zhou et al.[40], shows the Ni islands, formed on Cu crystal, dissociation by 12 eV Xe ions within impact angles of $\theta = 0 - 70^\circ$.

The above stated aspects of ion assistance growth can also be supported by the theoretical work done by Zhou et al [40]. They have calculated by molecular dynamics simulations of Ni layer growth, on Cu crystal, concurrent with Xe ion assistance that Xe ions with 12 eV ion energy are beneficial to rupture the Ni island nucleation when ion impingement angles are
Figure 3-12: Amorphous (a) to crystalline (b) transition of Sc (light) and Cr (dark) layers by increasing bilayer period N from, (a) 1.7 nm to (b) 3.4 nm.

(from the surface normal) within $0 - 70^\circ$ (Fig. 3-11). It has also been shown by calculations that there exist an optimization in ion energy and impact angle where maximum flattening of the layers with minimum intermixing can be achieved.

The positive effect of the low energy ion-bombardment has been discussed this far, but the ion-energy required to promote smoother growth may also induce some damages like: resputtering of deposited material, ion-implantation and bulk diffusion or intermixing at the onset of each layer formation. All these effects deteriorate the layer as well as the interface structure to a large extent, and hence also the optical performance is reduced. In one of the previous example, Fig. 3-7 (b), the lower reflectivity obtained for the sample grown with a homogeneous ion energy of 22 eV is believed to be the effect of an induced intermixing. In this regard, the two-stage modulated ion assistance, described in the previous section, have successfully treated the competing bulk diffusion and interface related issues for sub-nm thin multilayers.

It has also been realized that the ion-energy modulation of individual layers is more beneficial when amorphous layers are concerned. The surface roughness that arises with the growth of crystallites could be overcome by high initial ion energies $> 100$ eV but, at the cost of a large intermixing. Fortunately, sputtering of metals is more likely to promote an amorphous layer structure as long as individual layer thicknesses are below some critical limit for crystallization. Above the limit the amorphous layers convert into polycrystalline layers,
most probably due to the increasing densities and induced film stresses. This is shown in the TEM micrographs, Fig. 3-12 for two Cr/Sc multilayers having $\Lambda = 1.7$ nm, and 3.4 nm grown by similar parameters of modulated ion assistance. A shorter period (a), with individual layer thicknesses of about $\sim 0.7$ nm, have shown complete amorphous layer structure, while both Cr and Sc (b) have independently switched to polycrystalline as the layer thicknesses were doubled.
Chapter 4

Multilayer Characterization

There is no single technique which can look into hundreds of buried interfaces within sub-nm thin layers and give thorough compositional and structural information. However, multilayer investigation by a combination of characterization probes have shown to be useful to carry out the research objectives.

A comprehensive soft X-ray multilayer mirror characterization requires mirror performance tests for its maximum X-ray reflectivity as well as for the layer stability under thermal loads and mechanical stresses. These general properties of multilayers are directly associated with the local arrangement of atoms within the individual layers, and more intensely on the interface profiles. For that reason the focus here is to characterize the individual layer morphology i.e. whether layers are amorphous or have crystalline nature, and to analyze the structural appearance of individual and collective roughnesses of interfaces in a multilayer. This in turn, together with general reflectivity tests, have provided clues for overall mirror performance for different material systems. The techniques used for the characterization and the analyses made based on the results are included in this chapter.
4.1 Reflectivity Analysis

4.1.1 Hard X-ray (Cu-K\textsubscript{α}) Reflectivity

In-house powder diffraction is routinely utilized for calculating the deposition rates, for immediate optimization of the process conditions, and for structural characterization of multilayers. For these purposes a Philips powder diffractometer with a line-focused copper anode source (Cu-K\textsubscript{α}, \(\lambda = 0.154\) nm) operating at 0.8 kW, and a Xe gas filled proportional detector was used in low angle (0° – 15°) reflection geometry. For the primary optics side, i.e. the path from the X-ray tube exit to the sample, a Ni \(\beta\)-filter, a 1/4° divergence slit and a 2 mm brass mask was used for limiting and collimating the spot size on the sample. From the sample to the detector end, a 0.1 mm anti-scatter slit and a 1/4° divergence slit, similar to the primary side, was used as secondary optics. Depending on the source-sample-detector coupling two types of one-dimensional scans were made; specular reflectivity and diffuse scattering measurements.

Figure 4-1: A schematic representation of a typical scattering experiment. The incident X-rays with a wave vector \(k\) are scattered at an angle 2\(\theta\), and change into a reflected wave vector, \(k'\). The scanning in parallel or perpendicular direction of resultant vector \(q\) provides an in depth or lateral scattering information, respectively. The gray areas are inaccessible according to the X-ray reflection geometry.
Specular scans, or conventional $\omega - 2\theta$, scans were made by keeping the detector angle, $2\theta$, twice the incidence angle on the sample angle, $\theta(\omega = \theta)$. An easy way to visualize this arrangement is the wave vector transfer of incident, $k$, and reflected, $k'$, X-rays of wavelength $\lambda$ within reciprocal space, as illustrated in Fig. 4-1. If only elastic scattering is considered, the two wave vectors would have similar magnitudes and the resultant magnitude of the reciprocal scattering vector, $q = k - k'$ will be,

$$|q| = \frac{4\pi}{\lambda} \sin \theta. \quad (4.1)$$

Scanning along the surface normal in the direction of $q_z$, as a function of angle, $\theta$, will actually probe the chemical modulation sequence of the multilayer in the same direction as it was grown. A typical reflectivity curve obtained in such a scan is shown in Fig. 4-2 (a) for a Ti/Cr multilayer containing 100 bilayers. The main peak, labelled $m = 1$, is the first order Bragg reflection peak, originating from the multilayer periodicity, and can thus be used to determine $\Lambda$, by;

$$\Lambda = \frac{\lambda}{2 \sin \theta}. \quad (4.2)$$

Though more precise periodicity determination, without interfering refraction effects, require higher order Bragg reflections as well as implementing ‘modified’ Bragg’s law (Eq. 2.3) for X-rays as,

$$\Lambda = \frac{m\lambda}{2 \sin(\theta)\sqrt{1 + \frac{(1 - \delta)^2 - 1}{\sin^2 \theta}}}, \quad (4.3)$$

which after linearization become,

$$m^2 = 4 \frac{\Lambda^2}{\lambda^2} [\sin^2 \theta + \{(1 - \delta)^2 - 1\}]. \quad (4.4)$$

The multilayer period can be determined from the slope, $4 \frac{\Lambda^2}{\lambda^2}$, of the $\sin^2 \theta$ versus $m^2$ plot.

For most soft X-ray mirrors higher orders are difficult to get because usually mirrors are designed for the first order Bragg reflections, and according to Bragg’s law for such short periods as $\Lambda = 1$ to 2 nm, the first order multilayer peak already appears at $2\theta$ angles higher
Figure 4-2: (a) Cu-K$_\alpha$ reflectivity measurements for a Cr/Ti multilayer of $\Lambda = 1.3$ nm, containing 100 bilayers. The peak in the reflectivity curve corresponds to the first order Bragg reflection. The simulation (lower curve) yielded individual layer thicknesses of Ti and Cr and interface width of 0.46 nm. (b) Rocking curve scan around $m=1$. Gray area represents the diffusely scattered X-ray intensity, while enhancement in specular reflectivity appears in peak direction.

than 4$^\circ$, and since reflectivity ideally goes down as $1/q^4$ (for all materials) intensity is generally too low at angles higher than 15$^\circ$ to notify the peaks. Nevertheless, since $\bar{\eta} \approx 1$ the refraction effects can safely be neglected at these angles and, moreover, multilayer period and individual layer thicknesses can be simulated from the lower curve in the Fig. 4-2 with a reasonable precision. The visibility of Kiessig-fringes i.e. distinct destructive interference fringes from the finite thickness of the multilayer being a multiple of $\Lambda$ in the reflectivity curve (see Fig. 4-2) was used as a qualitative layer conformity measure when different multilayers were compared.

Knowledge about the lateral structure of multilayers is extracted by diffuse scattering (scattering in non-specular directions) recorded for a constant magnitude of $q$ with varying direction. It can be accomplished by rocking the sample, $\omega$, around one of the known multilayer reflections and keeping the detector position fixed. Scattered intensity around the specular direction is added up as background and appears as a raised shoulder, Fig. 4-2 (b), when sample was rocked in one or the other side of the specular peak. The shaded area in the figure represents the diffusely scattered intensity. A ratio of the diffuse-to-specular integrated intensities is a rough measure of overall lateral roughness of the multilayer structure. Unfortunately, in spite
of extensive efforts, comprehensive modelling for rocking-curve analysis is very complicated and need advancements in data simulations.

### 4.1.2 Soft X-ray Reflectivity

Development of soft X-ray mirrors cannot be achieved without testing them at the wavelength for which they are designed. During this project, mirror performance i.e. soft X-ray absolute reflectivity, was measured using the \textit{UE56/1-PGM} beamline at the synchrotron BESSY, Berlin, in Germany \[41\]. A triple-axis UHV reflectometer/diffractometer was connected to the exit slit of a beamline based on an elliptical undulator coupled with a plane grating monochromator (1200 lines/mm). Multilayers designed as normal incidence mirrors and as analyzers for polarized synchrotron radiation were investigated by four different measurements.

All four kinds of measurements are illustrated in Fig. 4-3, for a Cr/Ti multilayer (a, b, c) with \(N = 200\) (designed for normal-incidence), and a Cr/Ti multilayer (d, e) with \(N = 150\) (designed for the Brewster angle \(\sim 45^\circ\)). Following similar geometrical arrangements as of hard X-ray reflectivity (but at higher angles), specular reflectivity (a) and rocking (b) scans were obtained at Ti-2p absorption edge, \(E = 452\) eV. The specular scans were simulated to obtain information about the roughness which was used as a feed-back to improve the deposition process. Energy scans for (c), illustrious for synchrotrons, were performed for Cr/Ti multilayers in the energy range of 445 to 465 eV at fixed angles. The reflectometer control also facilitates to perform identical \(\omega - 2\theta\) scans for different energies over a required energy range and hence generate 2 dimensional, so called, Bragg scans. This allows to scan the Bragg-peak intensity and position with varying energy, and is very useful, especially close to the absorption edges where the reflectivity can change abruptly. Each data point, both in s- and p-polarized X-ray scans, in, Fig. 4-3 (d), represent the peak reflectivity in different \(\omega - 2\theta\) scans at the corresponding energy. For this particular sample, a maximum s-polarized reflectivity of 4.3\% was achieved at \(\theta = 42^\circ\) at the Ti-2p absorption edge, \(E = 454\) eV, shown in (e).

As mentioned before, roughness features measured by X-ray reflectivity varies non-linearly with operating X-ray wavelengths. In addition, X-ray beams are usually not perfectly monochromatic and collimated, and depending on the extent of these deviations the coherency of X-rays suffer in longitudinal and transverse directions respectively \[43\]. For grazing incidence measurements the longitudinal coherence of X-rays is more crucial to probe the lateral corre-
Figure 4-3: Types of measurements made with synchrotron radiation: (a) specular reflectivity scan, (b) diffuse scattering measurement around the specular peak, (c) energy scan, reflectivity peak occurred at the Ti-2p absorption edge. Above three measurements were made at near-normal incidence for a sample with N=200. (d) 2D Bragg scans, i.e. angle-energy scans for s- and p-polarized X-rays on a sample designed at Brewster angle, (e) A Bragg scan in 3D from which 2D Bragg scan can be derived. Angle and energy profiles are projected on the corresponding axis.
lations in a multilayer, while at normal incidence the vertical coherence is more important to determine the similar structure.

4.2 **In-situ** Annealing Using Hard X-ray Reflectivity

Thermal stability of multilayer systems at higher temperatures than growth temperatures (about room temperature) was measured by using XRR during *In-situ* annealing. The Philips X’pert $\theta - \theta$ MPD diffractometer with the same geometry as of the reflectivity scans was used to perform these tests. Samples were placed in a Büehler HDK 2.4 high-temperature high-vacuum chamber with a Be-window. For the study of the Cr/Ti multilayers with $N = 100$ the temperature was raised in steps of $100^\circ$C and samples were annealed for one hour at each temperature. As illustrated in the Fig. 4-4, the first order reflection, measured each time the temperature was raised, showed a continuous decrement till $400^\circ$C, whereafter the multilayer peak was splitted into two adjacent peaks which moved further apart on increasing the temperature while continuing lowering in the intensity. The Cr/Ti layer system have shown thermal stability only up to $\sim 100^\circ$C, which is a rather low value for most of the applications. In comparison, W/B$_4$ and Ni/V multilayers which have previously been tested were stable up to higher temperatures of $700^\circ$C and $350^\circ$C, respectively. This demonstrates the sensitivity of the multilayer which is a consequence of metastability of multilayer materials. A careful analysis of intensity, position and FWHM of the multilayer peak can be used to extract the structural and interfacial changes in multilayers at elevated temperatures.

4.2.1 High Resolution Transmission Electron Microscopy

Transmission electron microscopy, TEM, is the only available probe for direct imaging of multilayers and is thus performed, for structural characterization of individual layers inside the multilayers and to image the overall trend of roughness propagation when hundreds of interfaces are involved. TEM micrographs, included in this thesis are made by cross-sectional transmission electron microscopy (XTEM) using either a CM 20 UT microscope equipped with a LaB$_6$ filament, or a Tecnai 200 microscope with a field emission gun, FEG, both operated at 200 kV. Cross-sectional samples were prepared by mechanical thinning and polishing from both sides to a thickness of about 50 $\mu$m. Low-angle ($4^\circ$) ion milling, in either a BalTec RES
010 rapid ion etch operated at 8 kV, or a Gatan PIPS operated at 5 kV, was used to make the samples electron transparent. A final polishing stage, using low-energy ions at 2.5 kV, was applied to remove amorphous surface layers formed in the previous stage.

The microscopes were operated either in bright field or dark field imaging mode depending on if the unscattered or scattered electron beam was chosen for imaging, respectively. An example of the two imaging modes is shown in Fig. 4-5 from the same area in a Cr/Sc multilayer sample containing two distinct stacks with $\Lambda = 1.7$, and 3.4 nm. In the dark field mode an aperture was inserted such that no structural information with periodicity in the growth direction was transmitted to the image. Bright/dark stripes observed for Sc/Cr, respectively in a bright field mode, are mass diffraction contrasts. While in the dark field, which is composed of diffraction contrasts, the uniform gray image for the thinner layers indicates the absence of any short range order and therefore reflects the amorphous nature of these layers. Contrary to this, the appearance of bright and dark areas in the $\Lambda = 3.4$ nm region show the presence of crystallites for thicker layers. Reciprocal space imaging as well as electron diffraction patterns are also used to determine crystallite orientation with respect to the substrates.
4.3. INTERFACE CHARACTERIZATION

Figure 4-5: Two imaging modes of transmission electron microscopy from the same area in a sample. The bright field image was formed when unscattered electron beam was selected. Selection of scattered diffraction spots in back focal plane of the objective lens, by inserting an objective aperture have shown diffraction contrasts in image plane and is known as dark field image. Two multilayer periods, \( \Lambda = 1.7 \) and 3.4 nm are present in the sample.

4.3 Interface Characterization

4.3.1 Roughness

An inappropriate selection of substrate and multilayer materials from the materials physical and chemical aspects and/or the choice of deposition technique, process conditions as well as temporal and environmental changes can all be the cause of multilayer imperfections. For example, interdiffusion can intrinsically be introduced by chemical miscibility and thermal diffusion of the layer materials, during and after the deposition, and intermixing may be raised by extrinsic impact of energetic species on the growing surfaces during the growth process. It has also been realized that impurities incorporated during growth have remarkable effect on the surface energies of the sub nm thin layers [38] which in turn might play a crucial role in roughness propagation. Moreover, the overall roughness profile of a multilayer stack has an ultimate dependence on the total number of bilayers, the bilayer period, and the multilayer thickness ratio [25]. In addition, the roughness profile can not be generalized for all material combinations building a multilayer. A correlation and propagation of a few characteristic roughnesses probed in three metal-multilayer systems grown with low ion-energy bombardment
during magnetron sputtering is discussed here.

Based on the specular and diffuse X-ray scattering analysis a quantitative assessment about the prevailing roughnesses in few materials have been made. The electron microscopy, as a complementary real space probe have confirmed the reflectivity results in some cases, and provided extra information in other. For instance, a decrease in peak reflectance above 100 bilayers in the Cr/Ti multilayer system (as published in Paper I) was a manifestation of increasing accumulated roughness, supported by integrated diffuse scattering analysis of varying $N$ multilayers. However, the particular kind of roughnesses that have been accumulating with large $N$ could not be identified from the reflectivity curves. But, the TEM study performed on this system, Fig. 4-6 (a), have clearly shown an establishment of a low spatial frequency roughness after $N > 20$, and its accumulation on adding more bilayers while still having the local abruptness at interfaces. The imaging scale roughly depicts the $\xi \sim 20$ nm while the $\xi_\perp$ have extended at some areas to the height of the whole multilayer stack which is about 140 nm thick. Interestingly, this was not the case for very large $N = 600$ containing Cr/Sc multilayers as evident from the bright field micrograph in Fig. 4-6 (b). This specific sample was the one, that have shown maximum reflectance of 20.7% as mentioned in the first chapter. No signature of low spacial frequency roughness, at least on the scale of 200 nm, is seen. The layer perfection at the bottom near to the substrate (areas are magnified by high resolution images) is indeed superior to the middle and even more than the layers near to the surface. In spite of the evidence of roughness progression in X-ray reflectivity measurements with increasing $N$ in this system [11], it is not possible to specify any particular kind of irregularity with certainty from the TEM images. One hypothesis is that there might be an accumulating jaggedness as more layers were added and hence interfaces were locally distorted at atomic scales which, in turn, resulted in increased diffuse scattering. Owing to the amorphous nature, the imaging of such small details in multilayers is extremely difficult and requires proficiency in analytical TEM where scanning mode of electron transmission might help to reveal how high and low Z atoms arranged at the interfaces.

The TEM images in Fig. 4-7 show the material dependence on nano-structural evolution and roughness comparison for Cr/Ti, Cr/Sc and Ni/V multilayers. Each micrograph shows 4 different periods, and overall seven stacks on top of each other. Again the multilayer perfection is obvious for each $\Lambda$ in Cr/Sc as compared to Cr/Ti. Since, X-ray analysis have already shown
Figure 4-6: (a). A Cr/Ti multilayer with $\Lambda = 1.38$ nm, and containing 100 bilayers. The waviness seems to be accumulating with increasing N. (b) A Cr/Sc multilayer with $\Lambda = 1.59$ nm, containing 600 bilayers. There is no sign of waviness seen in the TEM image. The high resolution TEM images of the areas at the bottom, middle and top of the multilayer are also shown.
Figure 4-7: A transmission electron microscopic overview of multilayer structural differences between Cr/Ti, Cr/Sc and Ni/V layer systems. The thick and the dark stripe at the lower left corner of each view graph is a Si substrate. On top of the substrate seven multilayers with four different periods are stacked. Details of the Cr/Sc multilayer structure can be found in paper II.

a good layer conformity in the Ni/V multilayer system but also revealed a strong sensitivity to heat, the layer distortion in the image is believed to be an artifact of sample preparation or possibly magnetic interaction between Ni and electrons during imaging. This is an ongoing project and aims to explore: The impact of growth conditions on various roughnesses as have already been described in section 3.3 for the Cr/Ti layer system, the period dependent layer morphology and interface structure, and also the irreversibility or reproducibility of $\sigma$ and layer morphology in a multilayer regarding underlying roughness of the previous layer stack.

4.3.2 Intermixing and Interdiffusion

The increased $\sigma$ due to the increased intermixing or interdiffusion can easily be notified by reflectivity curve comparisons. Normally, intermixed interfaces lowers the specular peak reflectance with a simultaneous decrease in diffuse scattering. \textit{In-situ} XRR annealing also provides an extent of reflectivity decrease (or the thermal stability of a multilayer) with increase in thermal diffusion. As shown in Fig. 3-9, in a Mo/Si multilayer intermixing occurs at interfaces both due to the chemical reaction of the silicide formation and by high Z Mo momentum transfer. Intermixing, however is not detectable by TEM imaging for soft X-ray multilayers.
Chapter 5

Summary of the Results

Although, most of the work carried out during the last two years has been related to the periodic soft X-ray normal-incidence metal multilayers, also some side projects regarding non-periodic SXR and periodic EUV multilayers have been initiated during the course of time. This chapter includes a short summary of the projects together with their future perspective.

5.1 Cr/Sc Multilayer Condenser Mirrors

As mentioned earlier the main focus of the research has been to develop normal-incidence multilayer condenser mirrors for soft X-ray microscopy based on the line-emission sources. As a first attempt [11], for a soft X-ray microscopy system developed at KTH, Stockholm and based on laser-produced plasma source with one of the emission-line at \( \lambda = 3.374 \) nm, a condenser mirror has been realized. On the basis of previous theoretical and experimental understandings the Cr/Sc multilayer system was chosen for condenser mirror fabrication for this particular X-ray wavelength. A spherically polished glass with a diameter of 65 mm and a radius of curvature of 241 mm was used as a substrate. In order to obtain the multilayers with a uniform thickness all over the substrate an adjustable mask in front of each magnetron was placed. By controlling the deposition flux through the mask and also by altering the magnetic configuration, layer thickness uniformity (determined by multilayer peak position and intensity variation in
hard X-ray reflectivity measurements over the mirror radius), was optimized to about 0.6%. At-wavelength absolute reflectivity versus the mirror radius measurements made at Advanced Light Source (ALS) are shown in Fig. 5-1. An average reflectivity of 0.5% was measured at near-normal incidence while a peak reflectivity of 0.6% was obtained at the position 15 mm from the center. The two main factors limiting the reflectivity are believed to be the higher surface roughness ($\sigma \sim 0.48$ nm) of the glass substrates as compared to the Si substrates ($\sigma \sim 0.1$ nm), and the difficulty of ion-bombardment control on growing layers due to the insulating nature of these substrates. These obstacles can be overcome by using spherically polished Si substrates.

5.2 Cr/Ti Soft X-ray Multilayer Mirrors

Investigations of titanium based multilayer mirrors were initiated due to an expected establishment of a Ti-based Čerenkov X-ray source. In this regard Cr/Ti multilayer growth have been optimized for normal-incidence mirrors as well as for the multilayers intended to be used as polarizers. The ion energies and ion fluxes indispensable for interface smoothening and layer densification during two-stage growth were theoretically estimated and experimentally iterated to an optimum. In order to investigate the roughness effects associated with the increasing number of bilayers in this material system, a multilayer series was made. It is revealed that
possible number of periods in a multilayer that could be grown without dominant effects of evolving roughness in a Cr/Ti multilayer are limited to 100 bilayers. Paper 1 summarizes some of the results accomplished in this respect.

5.3 TEM Investigations

Investigations based on TEM imaging of Cr/Ti, Cr/Sc and Ni/V multilayer systems grown under varying conditions, is one of the main focus in this study. All three systems have been investigated with respect to multilayer period, $\Lambda$-dependent layer morphology and interfacial roughness. An example of ongoing research is shown in Fig. 4-7. Paper 2 in this thesis is based on the electron microscopy for structural characterization of Cr/Sc multilayers. An extension of such investigations on other material systems and usage of the analytical aspects of TEM will be of major interest in the future.

5.4 Mo/Si EUV Multilayer Mirrors

The curiosity of implementing the two-stage modulated ion assistance on comparatively thicker layers which is a requirement for EUV mirrors have motivated the growth of Mo/Si.\(^1\) The multilayer design and deposition parameters were optimized for maximum reflectance at $\lambda = 12.5$ nm. At-wavelength synchrotron radiation measurements were made at BESSY and a maximum reflectance of about 60% was achieved for a multilayer with $N = 50$ bilayers, as shown in Fig. 5-2. As compared to the existing maximum, which is more than 70%, this was a low reflectance. Nevertheless, during the optimization procedure ion-energy effects on layer formation of alternating high, (Mo), and low, (Si), $Z$ materials, mainly investigated through HXR, XRD and TEM, were of considerable interest. Based on the Mo/Si results and studies made for thicker $\Lambda$ in other layer systems, low-energy modulated ion assistance have proven to be more advantageous for creating abrupt and smooth interfaces for thinner layers. Results of this study (not included in this thesis) are currently in a manuscript form for a scientific publication.

\(^1\)This work was carried out in collaboration with Jordi Romero Mora as his internship project.
Figure 5-2: Reflectivity profile of a Mo/Si multilayer, measured at $\lambda = 12.5$ nm. The average interface width, $\sigma = 0.5$ nm, is determined by IMD simulations (not shown here).

5.5 Broadband, Cr/Sc Soft X-ray Multilayer Mirrors

A short project on fabrication of non-periodic thickness-graded, multilayers for normal-incidence broad band mirror applications in the water window have also been initiated.\textsuperscript{2} The Cr/Sc material system was considered for non-periodic mirror fabrication due to its known potential for soft X-ray multilayer mirrors. A graded layer thickness design, where the multilayer period was successively reduced, from 1.84 nm to 1.62 nm within 300 bilayers, from the substrate to the top of the multilayer stack was used. According to computer simulations [22] the expected wavelength dispersion was of $\Delta \lambda / \lambda = 0.1$, for such a mirror design. Although a low average reflectivity of 0.4% was achieved with $\Delta \lambda / \lambda \approx 0.2$, the energy scans measured at BESSY were in well agreement with the simulated wavelength-reflectivity profile.

\textsuperscript{2}Broad band mirror research was initiated by Kenneth Järrendahl and Peter Senneryd as a short project.
Bibliography


